



ARL-TR-8348 • APR 2018



# **The Gibbs Variational Method in Thermodynamics of Equilibrium Plasma: 1. General Conditions of Equilibrium and Stability for One-Component Charged Gas**

**by Michael Grinfeld and Pavel Grinfeld**

Approved for public release; distribution is unlimited.

## **NOTICES**

### **Disclaimers**

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.



# **The Gibbs Variational Method in Thermodynamics of Equilibrium Plasma: 1. General Conditions of Equilibrium and Stability for One-Component Charged Gas**

**by Michael Grinfeld**

*Weapons and Materials Research Directorate, ARL*

**Pavel Grinfeld**

*Drexel University, Philadelphia, PA*

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
<p>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p><b>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</b></p>					
1. REPORT DATE (DD-MM-YYYY) April 2018		2. REPORT TYPE Technical Report		3. DATES COVERED (From - To) 1 October 2017–13 March 2018	
4. TITLE AND SUBTITLE The Gibbs Variational Method in Thermodynamics of Equilibrium Plasma: 1. General Conditions of Equilibrium and Stability for One-Component Charged Gas				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Michael Grinfeld and Pavel Grinfeld				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) US Army Research Laboratory ATTN: RDRL-WMP-C Aberdeen Proving Ground, MD 21005				8. PERFORMING ORGANIZATION REPORT NUMBER  ARL-TR-8348	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT <p>In this report, we study the equilibrium and stability conditions of one-component charged gas using the Gibbs variational principles. We established the general equations allowing us to analyze the equilibrium conditions of the systems, which contain electrically charged constituents. For the sake of simplicity, technical transparency, and brevity, we limited ourselves to the systems containing the charges of a one sign. Our approach was based on the variational principles of Gibbs, which, in turn, are based on the concept of heterogeneous systems. The deduction of equations of equilibrium is based on the calculation of the first energy variation of the functionals with isoperimetric constraints. We established necessary conditions of thermodynamic stability of the corresponding equilibrium configurations and demonstrated how the concept of stability can be applied to the classical problem of thermodynamic inequalities. We also established the novel thermodynamic inequalities, which generalize the classical thermodynamic inequalities of Gibbs for the charges liquids or gases.</p>					
15. SUBJECT TERMS plasma, thermodynamics, Gibbs variational principles, plasma stability, equations of state					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT  UU	18. NUMBER OF PAGES  24	19a. NAME OF RESPONSIBLE PERSON Michael Grinfeld
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) (410) 278-7030

<b>Contents</b>	<b>iv</b>
<b>Acknowledgment</b>	
<b>1. Introduction</b>	<b>1</b>
<b>2. Gibbs Method in the Integral Form</b>	<b>1</b>
2.1 The Functional for One-Component Plasma	2
2.2 Basic Gibbs Variational Principle	5
2.3 First Variation and the Equilibrium Equations	5
<b>3. Second Variation and Stability Conditions</b>	<b>8</b>
3.1 Spectral Analysis of the Second Variation	9
3.2 Thermodynamic Inequalities	11
<b>4. Conclusion</b>	<b>15</b>
<b>5. References</b>	<b>16</b>
<b>Distribution List</b>	<b>17</b>

## **Acknowledgment**

---

The authors are sincerely and deeply grateful to the world-class expert in plasma physics, Dr Sergei Putvinski of Tri Alpha Energy, Inc., for his generosity in sharing with us his unique vision on plasma problems.

## 1. Introduction

---

The systems carrying electric charges in the form of plasma are widespread in nature. Various US Army-related applications deal with different plasmas. We do not dwell on any particular applications since we have analyzed theoretical issues equally relevant for any of those practical applications.

Basically, we address the general problems related to thermodynamics of plasma, including equilibrium and stability conditions for macroscopic systems containing components in a plasma state. Of course, these general issues have been addressed and revised in tens of classical textbooks, and certainly they will be addressed and revised in hundreds of textbooks to come. This keeps happening for 2 main reasons. First, the fundamentals of any discipline are full of striking inconsistencies and contradictions. These striking contradictions will never be fully avoided, although they stay dormant, sometimes, for decades and even centuries. Second, the number of promising and useful applications keeps growing and requires permanent revisions of fundamentals.

Thus, we do not address all fundamental problems and contradictions; this is simply impossible. Instead, we discuss the bare minimum of the thermodynamical tools—only those tools that are absolutely unavoidable when dealing with the problems of equilibrium and stability of systems containing gaseous plasmas.

There are 2 different approaches in thermodynamics, each having its own advantages and disadvantages. Josiah Willard Gibbs made the major contributions to each of them in his seminal treatises.<sup>1,2</sup> Current textbooks and monograph presentations of the thermodynamics of plasma mostly follow the Gibbs<sup>2</sup> basic principles of statistical thermodynamics and their subsequent development. Landau and Lifshitz<sup>3</sup> summarize those developments.

The approach of Gibbs,<sup>1</sup> based on the concept of heterogeneous systems and usage of variational principles, did not get enough attention. Here we apply the Gibbs variational method (as we understand it) for the analysis of the simplest possible systems containing ionized gases.

## 2. Gibbs Method in the Integral Form

---

As per the Gibbs general methodology, based on the concept of heterogeneous systems, we have to choose the energy and entropy functionals and specify the macroscopic degrees of freedom for the system. Consider a closed vessel containing a gas or liquid, the material particles of which carry charges.

Typically, the net charge of the system is close to zero. However, for the sake of brevity, we assume that all the charges are the same; for instance, electrons or negatively charged ions.

We use the Eulerian approach to describe liquid continuum media. Fortunately, the Eulerian description is the most convenient when dealing with both the thermodynamics of liquids and gases and also with electromagnetism.

## 2.1 The Functional for One-Component Plasma

---

Let  $\Omega$  be the volume inside the closed vessel. Let  $\rho(z)$  be the mass densities per unit volume of the gas (liquid) under study. Let  $\sigma$  be the charge density per unit mass. The charge density  $q$  per unit volume, then, is given by the relationship

$$q = \sigma\rho. \quad (1)$$

Let  $M$  and  $Q$  be the total mass and charge of the liquid, respectively. They are expressed by the following integrals over the domain occupied by the charged gaseous substance:

$$M = \int_{\Omega} d\Omega \rho(z), \quad Q = \int_{\Omega} d\Omega q(z) = \sigma M. \quad (2)$$

Let the  $\eta(z)$  be the entropy density per unit mass of the electric liquid, whereas  $S$  is the total entropy of the system; then we get

$$S = \int_{\Omega} d\Omega \rho \eta(z). \quad (3)$$

Let the  $e(z)$  be the spatial distribution of the internal energy density per unit mass of the electric liquid, whereas  $U$  is the total internal energy of the system, as follows:

$$U = \int_{\Omega} d\Omega \rho e(z). \quad (4)$$

Similarly, we introduce be the free energy density  $\psi(z)$  per unit mass of the electric liquid, whereas  $F$  is the total internal energy of the system and other thermodynamic functions.

The thermodynamics of the system will be completely defined when the internal energy density  $e$  is given as a function of the mass density  $\rho$  and the mass entropy density  $\eta$ , as follows:



$$e = e(\rho, \eta) . \quad (5)$$

Given the function  $e(\rho, \eta)$ , there is no need to separately choose any additional equations of state (EOSs); like, for instance, the pressure  $p$  or the absolute temperature  $T$  as functions of 2 macroscopic thermodynamic parameters. This information is already contained in the function  $e(\rho, \eta)$  and can be extracted from this function with the help of the formula

$$p(\rho, \eta) \equiv \rho^2 \frac{\partial e(\rho, \eta)}{\partial \rho}, \quad T(\rho, \eta) \equiv \frac{\partial e(\rho, \eta)}{\partial \eta}, \quad (6)$$

but not the other way around. Given the function  $p(\rho, \eta)$  we cannot recover from it the internal energy density function  $e(\rho, \eta)$ . That is why the function  $e(\rho, \eta)$  can be coined a complete EoS, whereas  $p(\rho, \eta)$  or  $T(\rho, \eta)$  are incomplete EoSs. So, there are several incomplete EoSs, none of which contains as much information as  $e(\rho, \eta)$ . However, several incomplete EoSs can contain altogether as much information as one complete EoS. The advantage of the incomplete EoSs is implied by the fact that they can be more easily extracted from physical experiments.

One can ask, “Is there only one complete EoS for given liquid substance?” The answer is negative. In particular, the free-energy density function  $\psi(\rho, T)$  contains as much information as the complete EoS function  $e(\rho, \eta)$ . Thus,  $\psi(\rho, T)$  is also a complete EOS on its own right.

The statistical thermodynamics provides a theoretical procedure allowing us to extract the complete EoS  $\psi(\rho, T)$  from data related to the spectrum of existing energy levels of the system. Calculation of the EoS still relies on an additional hypothesis that is not that easy to justify. Fortunately, some of the important qualitative facts can be extracted without full knowledge of the spectra.

The macroscopic Gibbs approach, based on the concept of heterogeneous systems, does not suggest any procedure for calculating the complete EoS from theoretical reasoning. Basically, with this approach the EoS should be extracted from specially designed experiments dictated by the basic thermodynamic principles, physical intuition, or a combination.

The peculiarity of the heterogeneous systems with plasma components consists in the necessity of taking into account the nonlocal electrostatic energy as an essential addition to the classical internal energy.

The classical, local, and additive internal energy can be presented in the form of a single integral over the domain  $\Omega$ , occupied by the substance under study. At the

same time, the electrostatic energy is different; it is nonadditive and nonlocal. Often it is presented in the form of a double integral over the domain occupied by the charged substance. The total electrostatic energy  $E_{elec}$  of the system we postulate in the following form of the integral,

$$E_{elec} = \frac{1}{2} \int_{\Omega} d\Omega \int_{\Omega} d\Omega^* \frac{q(z)q(z^*)}{|\vec{z} - \vec{z}^*|} = \frac{\sigma^2}{2} \int_{\Omega} d\Omega \int_{\Omega} d\Omega^* \frac{\rho(z)\rho(z^*)}{|\vec{z} - \vec{z}^*|}, \quad (7)$$

with a singular core (i.e., within the domain  $\Omega$  the integrand in Eq. 7 approaches infinity).

The singularity of the integrand creates a variety of technical difficulties. To avoid them the electrostatic energy can also be presented in the form of a single integral of the electrostatic field  $\vec{E}(z)$  without any singular core.

$$E_{elec} = \frac{1}{8\pi} \int_{Space} d\Omega |\vec{E}(z)|^2, \quad (8)$$

but the integral now spans over the whole space, not just part of it, occupied by the ionized substance. The field components  $E_i(z)$  are the gradients of the electrostatic potential  $\phi(z)$ .

$$E_i(z) = -\nabla_i \phi. \quad (9)$$

The theoretical electostatics were built based on the analogy with the earlier developed theory of self-gravitating celestial bodies. Still, many models of electrostatic systems are almost the same as the models of the systems with self-gravitation. For instance, the total gravitational energy  $E_{grav}$  of a self-gravitating body is typically postulated in the form

$$E_{grav} = -\frac{G}{2} \int_{\Omega} d\Omega \int_{\Omega} d\Omega^* \frac{\rho(z)\rho(z^*)}{|\vec{z} - \vec{z}^*|}. \quad (10)$$

We see that the electrostatic and gravitational energy are very similar but differ by the sign. The difference in the signs makes the physics of self-gravitating and self-repelling electrostatic systems completely different, although the mathematical tools used in both disciplines are almost identical.

In the following, we neglect the gravitational energy. We assume that the total energy of the system  $E_{tot}$  comprises the total internal energy  $E_{int}$  and total electrostatic energy given by the integrals

$$E_{tot} = E_{int} + E_{elec} = \int_{\Omega} d\Omega \rho e(\rho, \eta) + \frac{\sigma^2}{2} \int_{\Omega} d\Omega \int_{\Omega} d\Omega^* \frac{\rho(z) \rho(z^*)}{|\vec{z} - \vec{z}^*|}. \quad (11)$$

## 2.2 Basic Gibbs Variational Principle

---

Following Gibbs, we postulate that the thermodynamic and mechanical parameters of the equilibrium configuration deliver the minimum (more precisely, stationary value) to the total energy  $E_{tot}$ , given by Eq. 11. When talking about minimum, we must specify the mechanical and thermodynamical degrees of freedom of the system under consideration. Quite often, it is done by specifying allowable infinitesimal variations of certain parameters. We postulated that for our system the virtual variation of the mass density  $\delta\rho$  and entropy  $\delta\eta$  must keep the following integral amounts fixed:

$$\int_{\Omega} d\Omega \rho(z) = M, \quad (12)$$

and

$$\int_{\Omega} d\Omega \eta(z) = S. \quad (13)$$

Using the standard method of the Lagrange indefinite multipliers, we arrive at the following unconditional variational problem for the functional  $\Phi$  :

$$\Phi = \int_{\Omega} d\Omega \rho [e(\rho, \eta) - \Lambda - \Theta \eta] + \frac{\sigma^2}{2} \int_{\Omega} d\Omega \int_{\Omega} d\Omega^* \frac{\rho(z) \rho(z^*)}{|\vec{z} - \vec{z}^*|}, \quad (14)$$

where  $\Lambda$  and  $\Theta$  are the indefinite Lagrange multipliers.

## 2.3 First Variation and the Equilibrium Equations

---

The first variation of the functional  $\Phi$  reads

$$\delta\Phi = \int_{\Omega} d\Omega \left[ \left( (\rho e)_{\rho} - \Lambda_e + \sigma^2 \int_{\Omega} d\Omega^* \frac{\rho(z^*)}{|\vec{z} - \vec{z}^*|} \right) \delta\rho + \rho(e_{\eta} - \Theta) \delta\eta \right]. \quad (15)$$

Indeed, the functional  $\Phi$  can be presented as sum of 2 terms, as follows:

$$\Phi = I_{\Omega} + I_{\Omega\Omega}, \quad (16)$$

where

$$I_{\Omega} \equiv \int_{\Omega} d\Omega \rho \left[ e(\rho, \eta) - \Theta\eta - \Lambda \right] \quad (17)$$

and

$$I_{\Omega\Omega} \equiv \frac{\sigma^2}{2} \int_{\Omega} d\Omega \int_{\Omega} d\Omega^* \frac{\rho(z) \rho(z^*)}{|\vec{z} - \vec{z}^*|}. \quad (18)$$

Varying the expressions Eqs. 17 and 18, we get, respectively,

$$\delta I_{\Omega} \equiv \int_{\Omega} d\Omega \left[ \left( (\rho e)_{\rho} - \Theta\eta - \Lambda \right) \delta\rho + \rho(e_{\eta} - \Theta) \delta\eta \right] \quad (19)$$

and

$$\delta I_{\Omega\Omega} \equiv \sigma^2 \int_{\Omega} d\Omega \delta\rho(z) \int_{\Omega} d\Omega^* \frac{\rho(z^*)}{|\vec{z} - \vec{z}^*|}. \quad (20)$$

The denominator 2 in the relationship Eq. 20 disappeared because  $\rho$  in the integrand of Eq. 18 appears twice as  $\rho(z)$  and  $\rho(z^*)$ .

Adding the relationships Eqs. 19 and 20 we arrive at the required relationship Eq. 15 for the first variation of  $\delta\Phi$ .

Separating the independent variations  $\delta\rho$  and  $\delta\eta$  in Eq. 15, we arrive at the following conditions of the bulk equilibrium:

$$(\rho e)_{\rho} - \Theta\eta + \sigma^2 \int_{\Omega} d\Omega^* \frac{\rho(z^*)}{|\vec{z} - \vec{z}^*|} = \Lambda \quad (21)$$

and

$$e_\eta = \Theta . \quad (22)$$

Thus, we arrive at the system of 4 equations describing equilibrium configurations: 3 integral Eqs. 12, 13, and 21, and 1 algebraic Eq. 22, with respect to 4 unknowns: 2 spatial function  $\rho(z)$ ,  $\eta(z)$ , and 2 unknown constants  $\Lambda$  and  $\Theta$ . No boundary conditions are necessary for this system.

Let us introduce an electrostatic potential  $\phi(z)$ , defined as

$$\phi(\vec{z}) \equiv \sigma \int_{\Omega} d\Omega^* \frac{\rho(z^*)}{|\vec{z} - \vec{z}^*|} . \quad (23)$$

We then can rewrite the relationship Eq. 21 as

$$e(\rho, \eta) - \Theta \eta + \rho e_\rho(\rho, \eta) + \sigma \phi = \Lambda . \quad (24)$$

Using thermodynamic identities, Eq. 6, we can rewrite the relationship Eq. 24 as

$$e(\rho, \eta) - T\eta + \frac{p}{\rho} + \sigma \phi = \Lambda . \quad (25)$$

The relationship Eq. 25 can also be rewritten in terms of the free energy density  $\psi = e - \eta T$  as

$$\psi + \frac{p}{\rho} + \sigma \phi = \Lambda . \quad (26)$$

The relationships Eqs. 25 and 26 are equivalent from the standpoint of mathematics; however, depending on circumstances, one or another form appears to be more technically convenient.

In the absence of electric field the relationship Eq. 25 implies

$$e - T\eta + \frac{p}{\rho} = \Lambda . \quad (27)$$

The combination on the left-hand side of Eq. 27 is the specific value (per unit mass) of the so-called Gibbs thermodynamic potential, or the Grand thermodynamic potential of one-component liquid substance. For heterogeneous systems containing 2 one-component phases, this quantity also plays the role of the chemical potential  $\mu$  of the phases. In other words, the full equilibrium in the heterogeneous system, containing 2 one-component phases—not only the pressures and temperatures of the phases—should be equal ( $p_1 = p_2$ ,  $T_1 = T_2$ ), but

the chemical potentials of the phases ( $\mu_1 = \mu_2$ ) should also be equal. We do not proceed with this discussion in this paper; it will be done later. The interested reader should refer to the Grinfeld monograph.<sup>4</sup>

The relationship Eq. 25 shows that when dealing with electrostatic forces the additional term  $\sigma\phi$ , responsible for electrostatic interaction, should be included in the equilibrium equation and in the chemical potential  $\mu$ . This fact was known to Gibbs,<sup>1</sup> who established it from a different, less formal, and more intuitive reasoning. The advantage of the reasoning, presented here, is that it allows us to proceed with calculation of the second variation and, thus, to get the toll for analysis of stability conditions and not just the conditions of equilibrium. This is something that Gibbs was not able to accomplish in his time.

### 3. Second Variation and Stability Conditions

---

The main instrument in investigation of stability of heterogeneous systems is the second energy variation. If the second variation is negative for some allowable variations of the thermodynamics degrees of freedom, we can conclude that the equilibrium configuration under study is unstable.

By varying the relationship Eq. 15 one more time in the vicinity of equilibrium configuration, we arrive at the following formula of the second variation:

$$\delta^2\Phi(a, h) = \int_{\Omega} d\Omega (A_{\rho\rho}a^2 + 2A_{\rho\eta}ah + A_{\eta\eta}h^2) + \sigma^2 \int_{\Omega} d\Omega \int_{\Omega} d\Omega^* \frac{a(z)a(z^*)}{|\vec{z} - \vec{z}^*|}, \quad (28)$$

where

$$a(z) \equiv \delta\rho, \quad h(z) \equiv \delta\eta, \quad A_{\rho\rho} \equiv (\rho e)_{\rho\rho}, \quad A_{\rho\eta} \equiv (\rho e)_{\rho\eta}, \quad A_{\eta\eta} \equiv \rho e_{\eta\eta}. \quad (29)$$

For stability, the integral quadratic form  $\delta^2\Phi(a, h)$  should be nonnegative for the arbitrary variations satisfying the linear bulk constraints.

$$\int_{\Omega} d\Omega a(z) = 0, \quad \int_{\Omega} d\Omega h(z) = 0. \quad (30)$$

### 3.1 Spectral Analysis of the Second Variation

---

Consider the minimum of the second variation Eq. 28 under the isoperimetric constraints of Eq. 30 and the normalization condition

$$\int_{\Omega} d\Omega a^2(z) = 1. \quad (31)$$

As before, we arrive at the unconditional minimization of the functional

$$\Pi(a, h) \equiv \int_{\Omega} d\Omega \left[ \begin{aligned} & A_{\rho\rho} a^2 + 2A_{\rho\eta} ah + A_{\eta\eta} h^2 + \\ & \int_{\Omega} d\Omega^* \frac{a(z)a(z^*)}{|\vec{z} - \vec{z}^*|} - \alpha a - \beta h - \lambda a^2 \end{aligned} \right]. \quad (32)$$

In the relationship Eq. 32,  $\alpha$ ,  $\beta$ , and  $\lambda$  are the indefinite multipliers associated with the constraints Eqs. 30 and 31.

For the first variation of this functional we get

$$\frac{1}{2} \delta \Pi(a, h) \equiv \int_{\Omega} d\Omega \left[ \begin{aligned} & \left( (A_{\rho\rho} - \lambda)a + A_{\rho\eta}h + \int_{\Omega} d\Omega^* \frac{a(z^*)}{|\vec{z} - \vec{z}^*|} - \frac{1}{2}\alpha \right) \delta a + \\ & (A_{\rho\eta}a + A_{\eta\eta}h - \frac{1}{2}\beta) \delta h \end{aligned} \right]. \quad (33)$$

Thus, we arrive at the nonuniform linear bulk equations

$$(A_{\rho\rho} - \lambda)a + A_{\rho\eta}h + \int_{\Omega} d\Omega^* \frac{a(z^*)}{|\vec{z} - \vec{z}^*|} = \frac{1}{2}\alpha \quad (34)$$

and

$$A_{\rho\eta}a + A_{\eta\eta}h = \frac{1}{2}\beta. \quad (35)$$

We arrived at 5 equations, 2 Eqs. 30, plus Eqs. 31, 34, and 35, and 5 unknowns,  $a, h, \alpha, \beta, \lambda$ . Consider a solution of this system to be

$$a = a^{\circ}, h = h^{\circ}, \alpha = \alpha^{\circ}, \beta = \beta^{\circ}, \text{ and } \lambda = \lambda^{\circ}, \quad (36)$$

where the superscript “ $\circ$ ” refers to the equilibrium values of the corresponding parameters.

So, by definition, we get the following relationships:

$$\int_{\Omega} d\Omega a^{\circ 2}(z) = 1, \quad (37)$$

$$\int_{\Omega} d\Omega h^{\circ}(z) = 0, \int_{\Omega} d\Omega a^{\circ}(z) = 0, \quad (38)$$

$$(A_{\rho\rho} - \lambda)a^{\circ} + A_{\rho\eta}h^{\circ} + \int_{\Omega} d\Omega^* \frac{a^{\circ}(z^*)}{|\vec{z} - \vec{z}^*|} = \frac{1}{2}\alpha^{\circ}, \quad (39)$$

and

$$A_{\rho\eta}a^{\circ} + A_{\eta\eta}h^{\circ} = \frac{1}{2}\beta^{\circ}. \quad (40)$$

Let us consider Eqs. 38, 39, and 40 as a system of 4 linear equations with 4 unknowns  $a, h, \alpha$ , and  $\beta$ . This system is not only near but also uniform. Therefore, it always has a trivial solution  $a = h = \alpha = \beta = 0$ . This solution is of no interest to us since in view of Eq. 37 we need a solution of  $a^{\circ} \neq 0$ . So, we have to have a situation in which the system of Eqs. 17a, 18, 19 has multiple solutions. This is possible only for some special values of  $\gamma$ . We call them spectral values. In the following it is evident that the spectral values play a special role in the analysis of stability of equilibrium

For a spectral value  $\lambda^{\circ}$ , let us calculate the corresponding non-vanishing values of the unknowns  $a^{\circ}, h^{\circ}, \alpha^{\circ}$ , and  $\beta^{\circ}$ . Let us multiply Eq. 39 by  $a^{\circ}$ , Eq. 40 by  $h^{\circ}$ , and integrate the resulting relationships over the volume  $\Omega$ . Then, using Eq. 17, we get the relationships

$$\int_{\Omega} d\Omega A_{\rho\rho} a^{\circ 2}(z) + \int_{\Omega} d\Omega A_{\rho\eta} h^{\circ} a^{\circ}(z) + \int_{\Omega} d\Omega \int_{\Omega} d\Omega^* \frac{a^{\circ}(z) a^{\circ}(z^*)}{|\vec{z} - \vec{z}^*|} = \lambda^{\circ} \quad (41)$$

and

$$\int_{\Omega} d\Omega A_{\rho\eta}^e a^{\circ} h^{\circ} + \int_{\Omega} d\Omega A_{\eta\eta}^e h^{\circ 2} = 0. \quad (42)$$

Adding the relationships Eqs. 41 and 42, we get the relationship

$$\int_{\Omega} d\Omega (A_{\rho\rho} a^{\circ 2} + 2A_{\rho\eta} h^{\circ} a^{\circ} + A_{\eta\eta} h^{\circ 2}) + \int_{\Omega} d\Omega \int_{\Omega} d\Omega^* \frac{a^{\circ}(z) a^{\circ}(z^*)}{|\vec{z} - \vec{z}^*|} = \lambda^{\circ}. \quad (43)$$



Comparing Eq. 28 with Eq. 43, we get

$$\delta^2 \Phi(a^\circ, h^\circ) = \lambda^\circ. \quad (44)$$

In words, the relationship Eq. 44 says that the spectral values  $\lambda$  and the associated nontrivial solutions of the system Eqs. 38, 39, and 40 are equal to the extrema of the second energy variation of the system. Thus, we get the following necessary conditions of stability. For stability all the solutions of the system Eqs. 29, 31, 34, and 35, all the values of  $\lambda^\circ$  must be nonnegative.

We can reformulate this statement as the following:

For stability, all the spectral values  $\lambda$  of the linear uniform system

$$\int_{\Omega} d\Omega a^\circ(z) = 0, \quad \int_{\Omega} d\Omega h^\circ(z) = 0, \quad (45)$$

$$(A_{\rho\rho} - \lambda) a^\circ + A_{\rho\eta} h^\circ + \int_{\Omega} d\Omega^* \frac{a^\circ(z^*)}{|\vec{z} - \vec{z}^*|} - \frac{1}{2} \alpha^\circ = 0, \quad (46)$$

and

$$A_{\rho\eta} a^\circ + A_{\eta\eta} h^\circ - \frac{1}{2} \beta^\circ = 0, \quad (47)$$

with respect to the unknowns  $a, h, \alpha$ , and  $\beta$ , must be nonnegative. In the following we will be calling this statement the Stability Principle of Nonnegative Spectrum.

### 3.2 Thermodynamic Inequalities

---

The problem of stability and the stability principle of nonnegative spectrum has an immediate relation to the problem of thermodynamic inequalities. For the analysis of thermodynamical inequalities it is convenient to rewrite Eq. 46 as the following pair of equations:

$$(A_{\rho\rho} - \lambda) a^\circ + A_{\rho\eta} h^\circ + \phi^\circ - \frac{1}{2} \alpha^\circ = 0 \quad (48)$$

$$\nabla^i \nabla_i \phi^\circ + 4\pi a^\circ = 0. \quad (49)$$

Consider a shortwave spectrum of the system Eqs. 47–49 for which

$$\alpha^\circ = \beta^\circ = 0, \quad a^\circ = A e^{ik_m z^m}, \quad h^\circ = H e^{ik_m z^m}, \quad \phi^\circ = J e^{ik_m z^m}. \quad (50)$$

Then, Eqs. 47–49 imply the following system:

$$A_{\rho\eta} A + A_{\eta\eta} H = 0, \quad (51)$$

$$(A_{\rho\rho} - \lambda) A + A_{\rho\eta} H + J = 0, \quad (52)$$

and

$$-|\vec{k}|^2 J + 4\pi A = 0. \quad (53)$$

By eliminating the scalars  $H$  and  $J$  in Eqs. 51–53, we arrive at the single linear uniform equation

$$\left( A_{\rho\rho} - \lambda + 4\pi |\vec{k}|^{-2} - \frac{A_{\rho\eta}^2}{A_{\eta\eta}} \right) A = 0 \quad (54)$$

with respect to the remaining constant  $A$ .

Equation 54 always has the following trivial solution:

$$A = 0. \quad (55)$$

The nontrivial solutions exist only when the expression on the brackets in Eq. 54 vanishes. This obvious fact leads us to the following formula for the spectral values  $\lambda$  :

$$\lambda = \frac{A_{\rho\rho} A_{\eta\eta} - A_{\rho\eta}^2}{A_{\eta\eta}} + 4\pi |\vec{k}|^{-2}. \quad (56)$$

Thus, we arrive at the inequality

$$\frac{A_{\rho\rho}^e A_{\eta\eta}^e - A_{\rho\eta}^{e2}}{A_{\eta\eta}^e} + 4\pi |\vec{k}|^{-2} \geq 0. \quad (57)$$

If, instead of the normalization condition Eq. 31, we use

$$\int_{\Omega} d\Omega h^2(z) = 1, \quad (58)$$

then instead of the system Eqs. 51–53, we get the system

Approved for public release; distribution is unlimited.

$$A_{\rho\eta}A + (A_{\eta\eta} - \lambda)H = 0, \quad (59)$$

$$A_{\rho\rho}A + A_{\rho\eta}H + J = 0, \quad (60)$$

and

$$-\left|\vec{k}\right|^2 J + 4\pi A = 0. \quad (61)$$

System Eqs. 59–61 leads us to somewhat different spectral values of  $\lambda$ .

$$\lambda = \frac{A_{\eta\eta}A_{\rho\rho} - A_{\rho\eta}^2 + 4\pi\left|\vec{k}\right|^{-2} A_{\eta\eta}}{A_{\rho\rho} + 4\pi\left|\vec{k}\right|^{-2}}. \quad (62)$$

Thus, we arrive at the thermodynamic inequality

$$\frac{A_{\eta\eta}A_{\rho\rho} - A_{\rho\eta}^2 + 4\pi\left|\vec{k}\right|^{-2} A_{\eta\eta}}{A_{\rho\rho} + 4\pi\left|\vec{k}\right|^{-2}} \geq 0. \quad (63)$$

At last, let us consider the case of the normalization condition

$$\int_{\Omega} d\Omega (a^2 + \kappa^2 h^2) = 1. \quad (64)$$

In this case, we arrive at the spectral system

$$A_{\rho\eta}A + (A_{\eta\eta} - \kappa^2 \lambda)H = 0, \quad (65)$$

$$(A_{\rho\rho} - \lambda)A + A_{\rho\eta}H + J = 0, \quad (66)$$

and

$$-\left|\vec{k}\right|^2 J + 4\pi A = 0, \quad (67)$$

which can be rewritten in the following matrix form:

$$\begin{bmatrix} A_{\rho\eta} & A_{\eta\eta} - \kappa^2 \lambda & 0 \\ A_{\rho\rho} - \lambda & A_{\rho\eta} & 1 \\ 4\pi |\vec{k}|^{-2} & 0 & -1 \end{bmatrix} \begin{bmatrix} A \\ H \\ J \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}. \quad (68)$$

At  $|\vec{k}| \rightarrow \infty$ , the Eq. 68 reads

$$\begin{bmatrix} A_{\rho\eta} & A_{\eta\eta} - \kappa^2 \lambda & 0 \\ A_{\rho\rho} - \lambda & A_{\rho\eta} & 1 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} A \\ H \\ J \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}, \quad (69)$$

leading to the spectrum (secular) equation

$$\lambda^2 - \frac{A_{\eta\eta} + \kappa^2 A_{\rho\rho}}{\kappa^2} \lambda + \frac{A_{\eta\eta} A_{\rho\rho} - A_{\rho\eta}^2}{\kappa^2} = 0. \quad (70)$$

Equation 71 has the following discriminant  $\Delta$  :

$$\Delta \kappa^4 = \left( A_{\eta\eta} + \kappa^2 A_{\rho\rho} \right)^2 - 4 \kappa^2 \left( A_{\eta\eta} A_{\rho\rho} - A_{\rho\eta}^2 \right) = \left( A_{\eta\eta} - \kappa^2 A_{\rho\rho} \right)^2 + 4 \kappa^2 A_{\rho\eta}^2. \quad (71)$$

Obviously, the discriminant  $\Delta$  is always positive, and therefore the spectrum values  $\lambda$  are real. They will be nonnegative provided the following relationships are satisfied:

$$A_{\eta\eta} A_{\rho\rho} - A_{\rho\eta}^2 \geq 0 \quad (72)$$

and

$$A_{\eta\eta} + \kappa^2 A_{\rho\rho} \geq 0. \quad (73)$$

Since  $\kappa$  in the inequality Eq. 73 can be an arbitrary real constant, the positiveness of the Eigenvalues  $\lambda$  implies 2 independent inequalities:

$$A_{\eta\eta}^e \geq 0, \quad A_{\rho\rho}^e \geq 0. \quad (74)$$

Thus, in the asymptotics  $|\vec{k}|$  we arrive at the 3 classical thermodynamic inequalities of Eqs. 72, 73, and 74.

## 4. Conclusion

---

We established general equations allowing analysis of the equilibrium configurations of the systems containing electrically charged constituents. For the sake of simplicity, technical transparency, and brevity, we limited ourselves to the systems containing charges of a one sign. Our approach was based on the variational principles of Gibbs, which are, in turn, based on the concept of heterogeneous systems. The deduction of the equation of equilibrium is based on the calculation of the first energy variation of the functionals with isoperimetric constraints. We arrived at the system of 4 equations describing equilibrium configurations: 3 integral Eqs. 12, 13, and 21 and one algebraic Eq. 22 with respect to 4 unknown: 2 spatial functions  $\rho(z)$   $\eta(z)$ , and 2 unknown constants,  $\Lambda$  and  $\Theta$ . No boundary conditions are necessary for this system.

We then established the necessary conditions of thermodynamic stability of the corresponding equilibrium configuration. Our approach is based on the derivation and analysis of the second variation, which is given by the relationship Eq. 28, which uses the notation Eq. 29. The second variation appears in the quadratic integral form, which should be analyzed in conjunction with 2 linear integral constraints of the isoperimetric type in Eq. 30.

We demonstrated how the concept of stability can be applied to the classical problem of thermodynamic inequalities. We also established the novel thermodynamic inequalities Eqs. 57 and 63, which generalize the classical thermodynamic inequalities of Gibbs for the charges liquids or gases.

## 5. References

---

1. Gibbs JW. On the equilibrium of heterogeneous substances. Transactions of the Connecticut Academy of Arts and Sciences. 1874–1878;3:108–248, 343–524.
2. Gibbs JW. Elementary principles in statistical mechanics. New York (NY): Charles Scribner and Sons; 1902.
3. Landau LD, Lifshitz EM. Statistical physics. Oxford (UK): Butterworth-Heinemann; 1980.
4. Grinfeld MA. Thermodynamic methods in the theory of heterogeneous systems. London (UK): Longman; 1991.

1 DEFENSE TECHNICAL  
(PDF) INFORMATION CTR  
DTIC OCA

2 DIR ARL  
(PDF) IMAL HRA  
RECORDS MGMT  
RDRL DCL  
TECH LIB

1 GOVT PRINTG OFC  
(PDF) A MALHOTRA

9 JOHNS HOPKINS UNIV  
(PDF) K RAMESH

4 SANDIA NATL LAB  
(PDF) J NIEDERHAUS  
A ROBINSON  
C SIEFERT

39 ARL  
(PDF) RDRL D  
M TSCHOPP  
RDRL DP  
T BJERKE  
RDRL VTM  
M HAILE  
RDRL WM  
B FORCH  
J MCCAULEY  
S SCHOENFELD  
RDRL WML H  
B SCHUSTER  
RDRL WMM  
J BEATTY  
RDRL WMM B  
G GAZONAS  
D HOPKINS  
B LOVE  
B POWERS  
T SANO  
RDRL WMM E  
J SWAB  
RDRL WMM G  
J ANDZELM

RDRL WMP A  
S BILYK  
W UHLIG  
J CAZAMIAS  
P BERNING  
M COPPINGER  
K MAHAN  
C ADAMS  
RDRL WMP B  
C HOPPEL  
T WEERASOORIYA  
RDRL WMP C  
R BECKER  
D CASEM  
J CLAYTON  
M GREENFIELD  
R LEAVY  
J LLOYD  
S SEGLETES  
A TONGE  
C WILLIAMS  
S SATAPATHY  
A SOKOLOW  
RDRL WMP D  
R DONEY  
C RANDOW  
J RUNYEON  
G VUNNI

INTENTIONALLY LEFT BLANK.